

## Reactions Involving Fluoride Ion. Part 39.<sup>1</sup> Reactions of Perfluorinated Dienes with Oxygen and Sulphur Nucleophiles

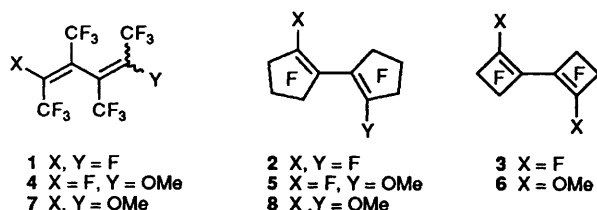
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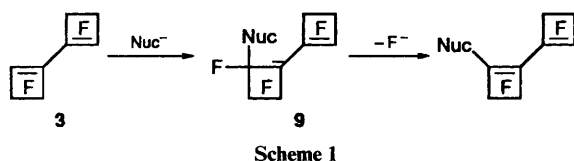
The order of reactivity of perfluorinated dienes towards methanol is  $3 > 2 \gg 1$  and the process is activated by release of angle strain. The diene **1** is hydrolysed to give perfluorotetramethyl-furan and the corresponding thiophene, is obtained by an analogous process using  $K_2S$ . Hydrolysis of compounds **2** and **3** yields diketones that are strong acids. Reactions of phenols and thiophenols with **1** give aryl ethers and sulfides and difunctional nucleophiles react with **1** to give potential polymer precursors.

In the preceding paper of this series we described efficient syntheses of the fluorinated dienes **1–3**, from oligomers which were themselves obtained from interaction of fluoride ion with some readily available fluorinated alkenes and cycloalkenes. Thus, a significant objective is achieved, which is to create simple methodology for obtaining chemically more sophisticated systems from simple fluorinated starting materials. This is crucially important to the area of polyfluorinated compounds that are wholly 'man-made' molecules. In this paper we describe the reactions of these new interesting electron-deficient dienes **1–3** with some oxygen and sulphur nucleophiles.

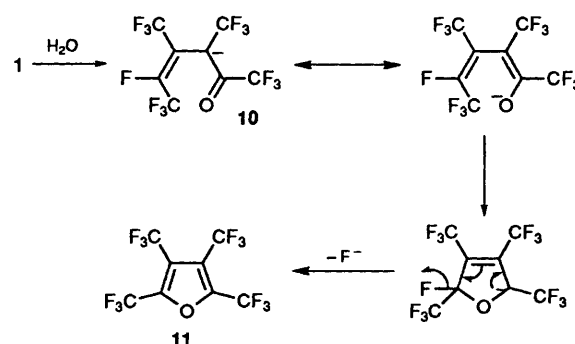
Reactions with methanol show a considerable range in reactivity; the diene **3** reacts exothermically with neutral methanol giving the bis-dimethyl ether **6**. Fluorinated alkenes are generally reactive to nucleophiles<sup>2</sup> but this remarkable level of reactivity is usually associated with perfluoroisobutene,<sup>3</sup> and it is comparatively rare that fluorinated systems will react with neutral methanol.<sup>4</sup>



Perfluorobicyclopentenyl **2** reacted with neutral methanol but only over a period of days, giving **5** and **8**, while the diene **1** required addition of base to promote reaction with methanol, giving **4** and **7**. Electronic effects are broadly equivalent for each of the dienes and, therefore, the dramatic difference in reactivity  $3 > 2 \gg 1$  is best accounted for on the basis of angle strain. Obviously, angle strain is relieved in the process  $3 \rightarrow 9$ , and the dramatic change in reactivity in the series **1–3** provides a nice illustration of this effect on reactivity (Scheme 1).

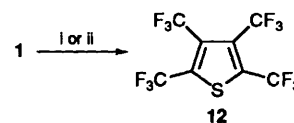


Hydrolysis is more complicated in that the diene **1** gave a product of cyclisation (Scheme 2), perfluorotetramethylfuran **11** and, indeed, this process occurs so readily in the presence of base that nucleophilic reactions on **1** frequently give **11** as an impurity in the product unless moisture is most rigorously excluded from the solvent.



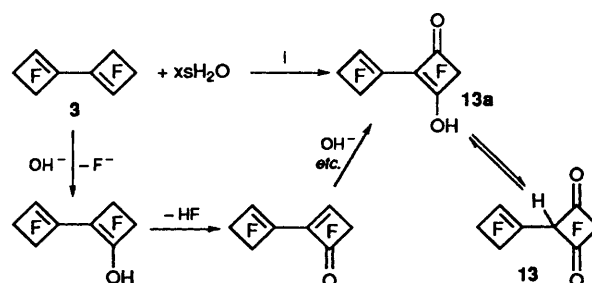
Scheme 2 Hydrolysis of the diene **1**

The process proceeds by initial vinylic displacement of fluorine and then the intermediate ion **10** clearly undergoes a rapid electrocyclic process, accompanied by elimination of fluoride ion to give **11**. The process is quantitative and represents a more direct route to the furan derivative **11** than previous procedures.<sup>5</sup> Analogous formation of the corresponding perfluorotetramethylthiophene **12** was less efficient but reaction of **1** with either potassium sulphide or thiourea gave **12**.



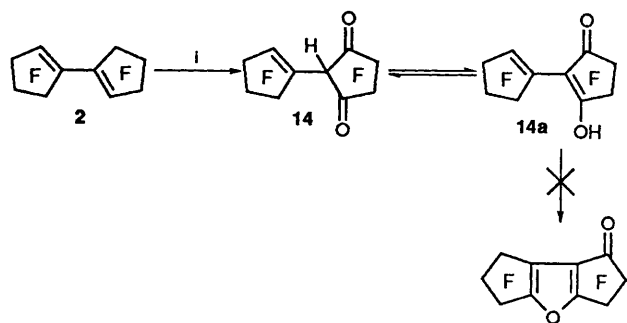
Scheme 3 Reagents and conditions: i,  $K_2S$ , DMF, room temp. (72%); ii,  $(NH_2)_2CS$ , MeCN, reflux (51%)

Reactions of the cyclic dienes **2** and **3** proceeded in a different manner. Hydrolysis of **2** and **3** in aqueous acetonitrile gave the corresponding diketones **14** and **13**, and the mechanism of formation of **13** is indicated in Scheme 4.



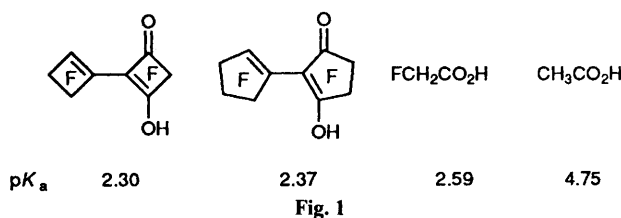
Scheme 4 Hydrolysis of the diene **3**. Reagents and conditions: i, MeCN, room temp.

The structure of **13** was derived partly from the observation of a resonance in the  $^{19}\text{F}$  NMR that could be attributed to  $\text{CF}=\text{C}$  and 3 resonances, of equal intensity, attributable to  $\text{CF}_2$ . Hydrolysis of **2** followed a similar mechanism to give the analogous product **14**.



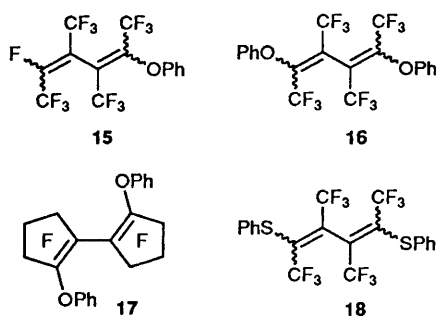
Scheme 5 Reagents and conditions: i,  $\text{H}_2\text{O}$ , MeCN, room temp.

Fluorinated diketones frequently exist principally in the enol form, e.g. hexafluoroacetylacetone,<sup>6</sup> and this is probably the case for both **13** and **14**. However, these compounds are very strong acids (see Fig. 1), and  $\text{pK}_\text{a}$  values are comparable to that of monofluoroacetic acid, although they do not approach that of the pseudo-aromatic compound squaric acid.



Indeed, we expected further loss of fluorine from **13** and **14** with base but, instead, neutralisation gave salts that were quite stable and could be isolated. The fact that cyclisation, analogous to that shown in Scheme 2, does not occur is most obviously attributable to the significant strain associated with the furan derivatives that would be obtained from **2** and **3**, analogous to **11**, obtained from **1**.

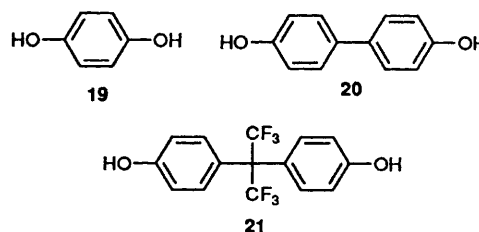
Reactions of the dienes **1** and **2** with phenol and thiophenol proceeded in an analogous manner and various mono-**15a-d** and di-substitution, **16a-c**, **19** and **18a-c**, products were obtained (see Experimental section).



These dienes are interesting monomers for polymerisation and we have made potential polymer precursors by reaction of the diene **1** with the difunctional derivatives **19-21**.

Reaction of the diene **1** with hydroquinone **19** and difunctional systems **20** and **21**, gave the disubstituted derivatives **23**, **24** and **25**, respectively (see Experimental section).

It is interesting to note that the only discernible isomers of these di-substituted products involved the all-*trans* relative arrangements of trifluoromethyl groups. Since we begin with a



mixture of *E,Z* and *Z,Z* isomers of the diene **1**, then these reactions are obviously subject to thermodynamic control of stereochemistry, with the bulky trifluoromethyl groups dominating the outcome. The product **25** reacted further with sodium methoxide, to give compound **26**, and this demonstrates that these intermediates could be used for a variety of block copolymer syntheses for systems containing trifluoromethyl groups.

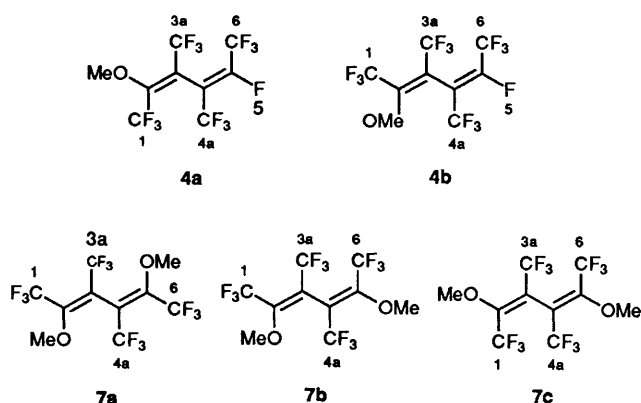
## Experimental

$^1\text{H}$  NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz or a Varian VXR400S spectrometer operating at 399.95 MHz.  $^{19}\text{F}$  NMR spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz.  $^{13}\text{C}$  NMR spectra were recorded on the Varian VXR400S spectrometer operating at 100.58 MHz. All spectra were recorded with tetramethylsilane and fluorotrichloromethane as internal references. *J* Values are given in Hz. GLC Mass spectra were recorded on a VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25 m cross-linked methyl silicone capillary column. All mass spectra were generated by electron impact.

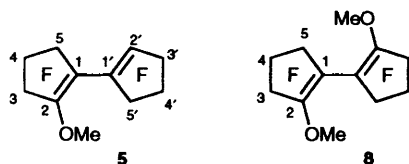
**Caution:** The dienes **1**, **2** and **3** should be assumed to be toxic.

**Reaction of the Diene 1 with Methanol.**—A mixture containing the diene **1** (2.0 g, 5.5 mmol), methanol (0.7 g, 22.2 mmol), sodium carbonate (0.9 g, 8.5 mmol), and acetonitrile (2 cm<sup>3</sup>) was stirred at room temperature for 7 d, after which volatile material was transferred *in vacuo* to a cold trap. The lower layer (1.4 g) was removed and shown by GLC to contain two products, which were separated by preparative scale GLC (column DNP, 110 °C), and identified as (1) (*Z,Z*)- and (*E,Z*)-2-methoxy-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene **4a, b** (90.2%). For the mixture (Found: C, 28.8; H, 0.7; F, 65.9.  $\text{C}_9\text{H}_9\text{F}_{13}\text{O}$  requires C, 28.9; H, 0.8; F, 66.0%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1750w (C=C), 1710w (C=C), 1385s (C-F) and 1360–1110s (C-F);  $m/z$  374 ( $\text{M}^+$ , 8%); for **4a**  $\delta_{\text{H}}$ (250 MHz;  $\text{CDCl}_3$ ) 3.9 (s, OCH<sub>3</sub>);  $\delta_{\text{F}}$ (235 MHz;  $\text{CDCl}_3$ ) –61.1 (3 F, s, 1-CF<sub>3</sub>), –61.7 (3 F, d,  $J_{4a,5}$  17.0, 4a-CF<sub>3</sub>), –64.1 (3 F, s, 3a-CF<sub>3</sub>), –69.1 (3 F, s, 6-CF<sub>3</sub>) and –106.5 (1 F, m, 5-CF); for **4b**  $\delta_{\text{H}}$ (250 MHz;  $\text{CDCl}_3$ ) 3.8 (s, OCH<sub>3</sub>);  $\delta_{\text{F}}$ (235 MHz;  $\text{CDCl}_3$ ) –56.8 (3 F, q,  $J_{1,3a}$  11.8, 1-CF<sub>3</sub>), –61.5 (3 F, d,  $J_{4a,5}$  16.9, 4a-CF<sub>3</sub>), –64.1 (3 F, s, 3a-CF<sub>3</sub>), –69.9 (3 F, d,  $J_{6,5}$  6-CF<sub>3</sub>), –109.2 (1 F, m, 5-CF) and (2) (*E,E*)-, (*E,Z*)- and (*Z,Z*)-2,5-dimethoxy-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene **7a, b, c** (9.8%). For the mixture (Found: C, 30.0; H, 0.7; F, 58.9.  $\text{C}_{10}\text{H}_6\text{F}_{12}\text{O}_2$  requires C, 31.1; H, 1.55; F, 59.1%);  $\nu_{\text{max}}/\text{cm}^{-1}$  17590w (C=C), 1710w (C=C), 1690w (C=C) and 1490–1080s (C-F);  $m/z$  386 ( $\text{M}^+$ , 20%); for **8a**  $\delta_{\text{H}}$ (250 MHz;  $\text{CDCl}_3$ ) 3.8 (s, OCH<sub>3</sub>);  $\delta_{\text{F}}$ (235 MHz;  $\text{CDCl}_3$ ) –57.2 (6 F, m, 3a- and 4a-CF<sub>3</sub>), –64.3 (6 F, q,  $J_{3a,1}$  11.6, 1- and 6-CF<sub>3</sub>); for **7b, c**  $\delta_{\text{H}}$ (250 MHz;  $\text{CDCl}_3$ ) 3.8 (s, OCH<sub>3</sub>);  $\delta_{\text{F}}$ (235 MHz;  $\text{CDCl}_3$ ) –61.3 and 61.1 (1 F, s, 3a- and 4a-CF<sub>3</sub>) and –64.0 and 64.9 (1 F, s, 1- and 6-CF<sub>3</sub>).

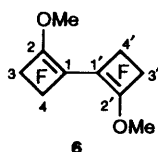
**Reaction of the Diene 2 with Methanol.**—The diene **2** (2.0 g, 5.2 mmol) and methanol (0.80 g, 25.0 mmol) were mixed at room temperature to give an immediate exothermic reaction.



The mixture was stirred and, after 48 h, a sample from the homogenous liquid was taken and shown by GLC to contain one product, which was identified as 2-methoxyperfluoro-1,1'-bicyclopent-1-enyl **5** (Found: C, 33.4; H, 0.8; F, 57.9.  $C_{11}H_3F_{13}O$  requires C, 33.2; H, 0.8; F, 62.1);  $\nu_{\max}/\text{cm}^{-1}$  1690m (C=C), 1660m (C=C), 1380s (C-F), 1320m (C-F), 1280m (C-F), 1210m (C-F), 1180s (C-F) and 1160s (C-F);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 4.2 (s,  $OCH_3$ );  $\delta_F$  (235 MHz;  $CDCl_3$ ) -105.6 (2 F, s, 5- $CF_2$ ), -107.8 (2 F, s, 5'- $CF_2$ ), -113.0 (2 F, s, 3- $CF_2$ ), -114.4 (1 F, m, 2'-CF), -119.5 (2 F, d,  $J_{6,7}$  14.0, 3'- $CF_2$ ), -129.7 (2 F, s, 4- $CF_2$ ), -130.5 (2 F, s, 4'- $CF_2$ );  $m/z$  398 ( $M^+$ , 100%). The reaction was allowed to continue for 10 d, after which solvent was removed to yield a crystalline white solid. This was purified by vacuum sublimation and identified as 2,2'-dimethoxyperfluoro-1,1'-bicyclopent-1-enyl **8**, m.p. 54 °C (Found: C, 35.0; H, 1.2; F, 55.7.  $C_{12}H_2F_{12}O_2$  requires C, 35.1; H, 1.5; F, 55.6%);  $\nu_{\max}/\text{cm}^{-1}$  1690 (C=C), 1640m (C=C), 1350s (C-F), 1245s (C-F), 1205m (C-F), 1130 (C-F) and 1115s (C-F);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 4.1 (s,  $OCH_3$ );  $\delta_F$  (235 MHz;  $CDCl_3$ ) -106.5 (1 F, s, 5- $CF_2$ ), -115.6 (1 F, s, 3- $CF_2$ ) and -131.0 (1 F, s, 4- $CF_2$ );  $m/z$  410 ( $M^+$ , 100%).

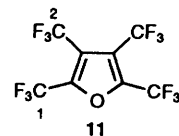


**Reaction of the Diene 3 with Methanol.**—Addition of the diene **3** (1.27 g, 4.4 mmol) to methanol (0.64 g, 20.0 mmol) gave an immediate exothermic reaction, with the formation of a white solid within 1 h. Solvent was then removed, and the residue sublimed *in vacuo* to give a white solid which was identified as 2,2'-dimethoxyperfluoro-1,1'-bicyclobut-1-enyl **6** (1.00 g, 73%), m.p. 52 °C (Found: C, 38.5; H, 1.9; F, 49.4.  $C_{10}H_6F_8O_2$  requires C, 38.7; H, 1.94; F, 49.0);  $\nu_{\max}/\text{cm}^{-1}$  1640s (C=C), 1380s (C-F), 1295s (C-F), 1120s (C-F), 1090m (C-F);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 4.1 (s,  $OCH_3$ );  $\delta_F$  (235 MHz;  $CDCl_3$ ) -111.7 (4 F, m, 4- $CF_2$ ) and -114.7 (4 F, m, 3- $CF_2$ );  $m/z$  310 ( $M^+$ , 76%).

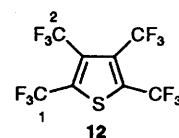


**Perfluorotetramethylfuran 11.**—A mixture containing the diene **1** (3.0 g, 8.3 mmol), water (0.2 g, 11.1 mmol), potassium carbonate (2.3 g, 16.7 mmol) and acetonitrile (20  $\text{cm}^3$ ) was stirred at room temperature for 14 d. Volatile material was transferred *in vacuo* to a cold trap and more water (20  $\text{cm}^3$ ) was

added to it. The lower layer was removed and purified by distillation to yield the title compound **11** (2.3 g, 54%), b.p. 101–103 °C (lit.,<sup>5</sup> 104–105 °C);  $\nu_{\max}/\text{cm}^{-1}$  1420w (C=C) and 1300s–1200s (C-F);  $\delta_F$  (235 MHz;  $CDCl_3$ ) -57.62 (1 F, m,  $CF_3$ ) and -62.40 (1 F, m,  $CF_3$ );  $m/z$  340 ( $M^+$ , 44%) and 321 (100).

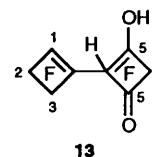


**Perfluorotetramethylthiophene 12.**—A mixture containing the diene **1** (10.0 g, 27.6 mmol), potassium sulphide (4.5 g, 40.9 mmol) and DMF (25  $\text{cm}^3$ ) was stirred at room temperature for 14 d. Volatile material was transferred *in vacuo* to a cold trap and water (25  $\text{cm}^3$ ) was added to it. The lower layer was removed and purified by distillation to yield the title compound **12** (3.7 g, 38%), b.p. 134–135 °C (lit.,<sup>7</sup> 134–135 °C);  $\nu_{\max}/\text{cm}^{-1}$  1240s–1200s (C-F);  $\delta_F$  (235 MHz;  $CDCl_3$ ) -54.12 (1 F, m,  $CF_3$ ) and -56.00 (1 F, m,  $CF_3$ );  $m/z$  356 ( $M^+$ , 81%) and 337 (100).



**Reaction of the Diene 1 with Thiourea.**—A mixture containing the diene **1** (2.0 g, 5.5 mmol), thiourea (0.5 g, 6.6 mmol) and acetonitrile (20  $\text{cm}^3$ ) was heated under reflux for 16 h. Volatile material was transferred *in vacuo* to a cold trap and water (30  $\text{cm}^3$ ) was added to it. The lower layer was removed and purified by distillation to give perfluorotetramethylthiophene **12** (1.0 g, 51%), which was identified by comparison of the  $^{19}F$  NMR spectrum with that of an authentic sample (see earlier).

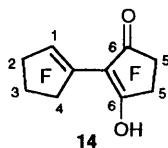
**Reaction of the Diene 3 with Water.**—A mixture of the diene **3** (1.15 g, 4.0 mmol), acetonitrile (7  $\text{cm}^3$ ) and distilled water (1.33 g, 74.0 mmol), was stirred at room temperature for 1 d, after which the solvent was removed. The residual solid sublimed *in vacuo*, to give a white hygroscopic solid which was identified as 4,4-difluoro-3-hydroxy-2-(perfluorocyclobut-1-enyl)but-2-enone **13** (0.80 g, 76%) (Found: C, 36.3; H, 0.8; F, 53.2.  $C_{10}HF_{11}O_2$  requires C, 36.6; H, 0.4; F, 53.8%);  $\nu_{\max}/\text{cm}^{-1}$  3450w (OH), 1800w (C=C), 1650s (C=O) and 1410–1110s (C-F);  $\delta_F$  (376 MHz;  $CD_3CN$ ) -102.8 (1 F, t, 1-CF), -113.4 (2 F, br s, 4- $CF_2$ ), -115.4 (2 F, 3- $CF_2$ ) and -117.5 (2 F, 2- $CF_2$ );  $m/z$  262 ( $M^+$ , 14%).



NB: Proton exchanges with deuterium

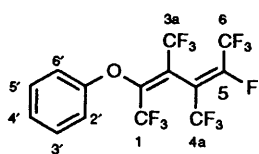
**Reaction of the Diene 2 with Water.**—A mixture of the diene **2** (0.70 g, 1.8 mmol), distilled water (1.05 g, 58.3 mmol) and acetonitrile (7  $\text{cm}^3$ ) was stirred at room temperature for 3 d, after which solvent was removed. The residue was sublimed *in vacuo*, to give a white solid which was identified as tetrafluoro-3-hydroxy-2-(perfluorocyclopent-1-enyl)cyclopent-2-enone **14** (0.50 g, 77%) (Found: C, 33.0; H, 0.3; F, 53.0.  $C_{10}HF_{11}O_2$  requires C, 32.5; H, 0.3; F, 53.7%);  $\nu_{\max}/\text{cm}^{-1}$  3450w (OH), 1740w (C=C), 1600s (C=O), 1350m (C-F) and 1210–1090s (C-F);  $\delta_F$  (376 MHz;  $CD_3CN$ ) -107.9 (2 F, d,  $J_{FF}$  10.8, 4- $CF_2$ ), -115.1 (1 F, m, 1-CF), -120.4 (2 F, d,  $J_{FF}$  14.4, 2- $CF_2$ ), -125.2

(4 F, s, 5-CF<sub>2</sub>) and -131.9 (2 F, br s, 3-CF<sub>2</sub>); *m/z* 362 (M<sup>+</sup>, 14%).

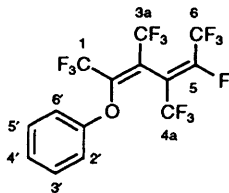


NB: Proton exchanges with deuterium

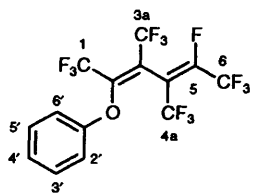
**Reaction of the Diene 1 with Phenol.**—A mixture containing the diene **1** (5.0 g, 13.8 mmol), phenol (1.9 g, 20.2 mmol), dry potassium fluoride (4.8 g, 82.8 mmol) and acetonitrile (75 cm<sup>3</sup>) was stirred at room temperature for 7 d. The resulting mixture was poured into water (200 cm<sup>3</sup>) and the organic products were extracted into diethyl ether and the extract dried (MgSO<sub>4</sub>), filtered and evaporated. The more volatile components were separated by distillation (52–54 °C, 10 mmHg) to give a colourless oil (2.8 g, 46%) which was shown to be a mixture (38:6:5:1) of (Z,Z)-, (Z,E)-, (E,E)- and (E,Z)-2-phenoxy-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene **15a–d**. For the mixture (Found: C, 38.7; H, 1.1; F, 56.9. C<sub>14</sub>H<sub>5</sub>F<sub>13</sub>O requires C, 38.55; H, 1.2; F, 56.6%;  $\nu_{\max}/\text{cm}^{-1}$  3040w (ArH), 1710w (C=C), 1660m (Ar), 1600m (Ar), 1490m (Ar), 1380 (C–F) and 1290s–1160s (C–F); *m/z* 436 (M<sup>+</sup>, 22%); for **15a**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.89 (2 H, m, 2'- and 6'-ArH), 7.09 (1 H, m, 4'-ArH) and 7.25 (2 H, m, 3'- and 5'-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -61.10 (3 F, s, 1-CF<sub>3</sub>), -61.12 (3 F, d, *J*<sub>4a,5</sub> 20.3, 4a-CF<sub>3</sub>), -62.31 (3 F, q, *J*<sub>3a,1</sub> 1.9, 3a-CF<sub>3</sub>), -69.59 (3 F, d, *J*<sub>6,5</sub> 4.9 of q, *J*<sub>6,3a</sub> 1.9 6-CF<sub>3</sub>), -105.19 (1 F, q, *J*<sub>5,4a</sub> 15.5 of q, *J*<sub>5,6</sub> 8.1, 5-CF); for **15b**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.82 (2 H, m, 2'- and 6'-ArH), 7.11 (1 H, m, 4'-ArH) and 7.27 (2 H, m, 3'- and 5'-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -60.48 (3 F, d, *J*<sub>4a,5</sub> 15.4, 4a-CF<sub>3</sub>), -60.99 (3 F, s, 1-CF<sub>3</sub>), -62.70 (3 F, q, *J*<sub>3a,1</sub> 11.9, 3a-CF<sub>3</sub>), -70.49 (3 F, d, *J*<sub>6,5</sub> 8.6, 6-CF<sub>3</sub>), -107.08 (1 F, q, *J*<sub>5,4a</sub> 14.7 of q, *J*<sub>5,6</sub> 8.7, 5-CF); for **15c**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.89 (2 H, m, 2'- and 6'-ArH), 7.07 (1 H, m, 4'-ArH) and 7.26 (2 H, m, 3'- and 5'-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -57.21 (3 F, d, *J*<sub>4a,5</sub> 10.4 of q, *J*<sub>4a,6</sub> 10.4 of q, *J*<sub>4a,3a</sub> 2.6, 4a-CF<sub>3</sub>), -58.29 (3 F, q, *J*<sub>1,3a</sub> 11.7 of q, *J*<sub>1,4a</sub> 1.9, 1-CF<sub>3</sub>), -63.39 (3 F, s, 3a-CF<sub>3</sub>), -69.23 (3 F, q, *J*<sub>6,3a</sub> 10.7 of d, *J*<sub>6,5</sub> 7.7, 6-CF<sub>3</sub>), -101.33 (1 F, m, 5-CF); for **15d**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.91 (2 H, m, 2'- and 6'-ArH), 7.06 (1 H, m, 4'-ArH) and 7.23 (2 H, m, 3'- and 5'-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -56.94 (3 F, d, *J*<sub>4a,5</sub> 10.7 of q, *J*<sub>4a,6</sub> 10.7 of q, *J*<sub>4a,3a</sub> 2.9, 4a-CF<sub>3</sub>), -58.29 (3 F, s, 1-CF<sub>3</sub>), -58.33 (3 F, q, *J*<sub>3a,1</sub> 2.5, 3a-CF<sub>3</sub>), -69.11 (3 F, q, *J*<sub>6,4a</sub> 10.5 of d, *J*<sub>6,5</sub> 7.5, 6-CF<sub>3</sub>) and -102.49 (1 F, m, 5-CF).



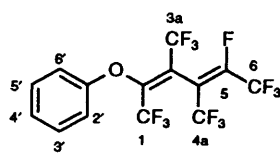
15a



15b



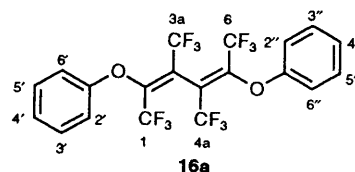
15c



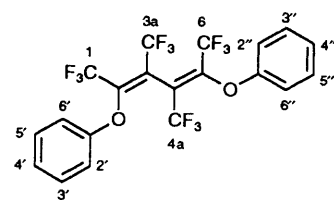
15d

The remaining solid was purified by sublimation followed by recrystallisation from diethyl ether–hexane to give a waxy solid

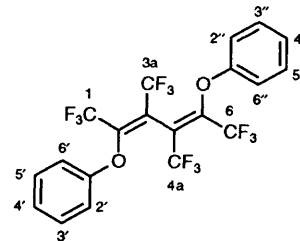
(3.3 g, 47%) which was shown to be a mixture (5:4:1) of (Z,Z)-, (E,Z)- and (E,E)-2,5-diphenoxy(3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene **16a–c**. For the mixture (Found: C, 47.0; H, 2.0; F, 44.2. C<sub>20</sub>H<sub>10</sub>F<sub>12</sub>O<sub>2</sub> requires C, 47.1; H, 2.0; F, 44.7%);  $\nu_{\max}/\text{cm}^{-1}$  3020w (Ar-H), 1660m (Ar), 1600s (Ar), 1490 (Ar) and 1360vs–1140vs (C–F); *m/z* 510 (M<sup>+</sup>, 10%); for **16a**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.95 (2 H, m, 2'-, 2'', 6'- and 6''-ArH), 7.10 (1 H, m, 4'- and 4''-ArH) and 7.29 (2 H, m, 3'-, 3'', 5'- and 5''-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -60.25 (1 F, q, *J*<sub>3a,1</sub> 2.3, 3a- and 4a-CF<sub>3</sub>), -61.80 (1 F, q, *J*<sub>1,3a</sub> 1.9, 1- and 6-CF<sub>3</sub>); for **16b**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.77 (2 H, m, 2'- and 6'- or 2''- and 6''-ArH), 6.92 (2 H, m, 2'- and 6'- or 2''- and 6''-ArH), 7.12 (1 H, m, 4'- or 4''-ArH), 7.15 (1 H, m, 4'- or 4''-ArH) and 7.27 (4 H, m, 3'-, 3'', 5'- and 5''-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -57.15 (1 F, q, *J*<sub>3a,1</sub> 10.9 of q, *J*<sub>3a,6</sub> 2.3, 3a-CF<sub>3</sub>), -59.56 (1 F, s, 4a-CF<sub>3</sub>), -62.04 (3 F, q, *J*<sub>1,3a</sub> 12.0, 1-CF<sub>3</sub>) and -63.34 (3 F, q, *J*<sub>6,3a</sub> 3.0, 6-CF<sub>3</sub>); for **16c**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.87 (2 H, m, 2'-, 2'', 6'- and 6''-ArH), 7.02 (1 H, m, 4'- and 4''-ArH) and 7.24 (2 H, m, 3'-, 3'', 5'- and 5''-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) 56.43 (1 F, q, *J*<sub>3a,1</sub> 11.3, 3a- and 4a-CF<sub>3</sub>), -62.31 (1 F, q, *J*<sub>1,3a</sub> 12.0, 1- and 6-CF<sub>3</sub>).



16a



16b



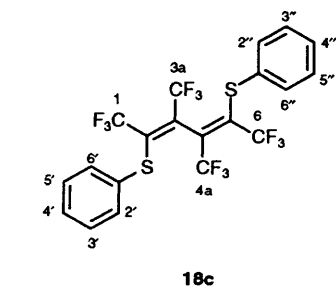
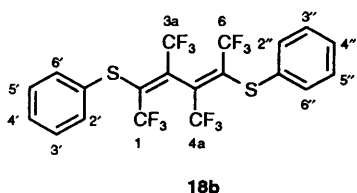
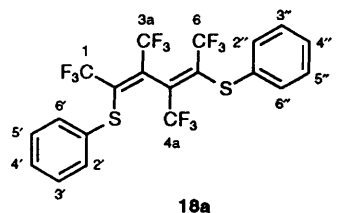
16c

**Reaction of the Diene 2 with Phenol.**—A mixture containing the diene **2** (1.0 g, 2.6 mmol), phenol (0.4 g, 4.3 mmol), dry potassium fluoride (1.0 g, 17.2 mmol) and acetonitrile (20 cm<sup>3</sup>) was stirred at room temperature for 7 d. The product was poured into water (100 cm<sup>3</sup>) and the organic components were extracted into diethyl ether, dried (MgSO<sub>4</sub>), filtered and evaporated. Sublimation of the residue gave 2,2'-diphenoxyperfluoro-1,1'-bicyclopent-1-enyl **17** (0.8 g, 58%), m.p. 79–82 °C (Found: C, 49.8; H, 2.1; F, 43.1. C<sub>22</sub>H<sub>10</sub>F<sub>12</sub>O<sub>2</sub> requires C, 49.5; H, 1.9; F, 42.7%);  $\nu_{\max}/\text{cm}^{-1}$  3020w (ArH), 1640m (Ar), 1590m (Ar), 1400m–980m (C–F);  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 7.25 (m, ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) -106.90 (1 F, s, CF<sub>2</sub>), -116.93 (1 F, s, CF<sub>2</sub>) and -131.13 (1 F, s, CF<sub>2</sub>); *m/z* 572 (M<sup>+</sup>, 13%).

**Reaction of the Diene 1 with Thiophenol.**—Thiophenol (0.9 g, 8.2 mmol) was slowly added to a stirred suspension of sodium hydride (0.2 g, 8.3 mmol) in DMF (20 cm<sup>3</sup>), and the solution was left at room temperature for 30 min. The diene **1** (2.0 g, 5.5

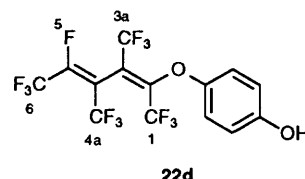
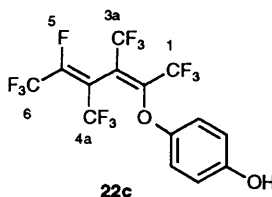
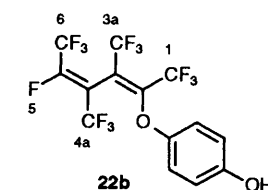
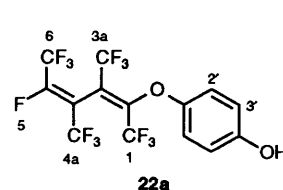


mmol) was then added to the mixture which was then stirred for 2 h. The resulting mixture was poured into slightly alkaline water (100 cm<sup>3</sup>) and the organic products were extracted into diethyl ether and the extracts dried (MgSO<sub>4</sub>) and filtered. The ether was removed from the filtrate by distillation and the residual solid was first sublimed and then recrystallised from acetone to give a solid (1.3 g, 59%) which was shown to be a mixture (9:8:3) of (E,Z)-, (Z,Z)- and (E,E)-2,5-diphenylsulfanyl-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene **18a-c**. For the mixture (Found: C, 44.0; H, 2.2; F, 41.5; S, 12.7. C<sub>20</sub>H<sub>10</sub>F<sub>12</sub>S<sub>2</sub> requires C, 44.3; H, 1.9; F, 42.0; S, 11.8%);  $\nu_{\max}/\text{cm}^{-1}$  3010w (ArH), 1590w (Ar), 1490w (Ar), 1400w (Ar) and 1300m–1160s (C–F);  $m/z$  433 (M<sup>+</sup>, 30%); for **18a**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 7.22 (1 H, m, 4'- or 4''-ArH), 7.23 (1 H, m, 4'- or 4''-ArH), 7.30 (2 H, m, 3'- and 5'- or 3'' and 5''-ArH), 7.37 (2 H, m, 3'- and 5'- or 3'' and 5''-ArH), 7.49 (2 H, m, 2'- and 6'- or 2'' and 6''-ArH) and 7.50 (2 H, m, 2'- and 6'- or 2'' and 6''-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) –56.43 (1 F, q,  $J_{1,3a}$  14.3, 1-CF<sub>3</sub>), –56.57 (1 F, s, 4a-CF<sub>3</sub>), –57.31 (1 F, q,  $J_{3a,1}$  13.6 of q,  $J_{3a,6}$  4.2 of q,  $J_{3a,4a}$  1.6, 3a-CF<sub>3</sub>) and –57.75 (1 F, q,  $J_{6,3a}$  4.1, 6-CF<sub>3</sub>); for **18b**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 7.21 (1 H, m, 4'- and 4''-ArH), 7.36 (2 H, m, 3'-, 3'', 5'- and 5''-ArH) and 7.46 (2 H, m, 2'-, 2'', 6'- and 6''-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) –57.27 (1 F, pseudo-sept,  $J_{3a,1+4a}$  2.4, 3a- and 4a-CF<sub>3</sub>), –57.88 (1 F, pseudo-sept,  $J_{1,3+4a}$  2.4, 1- and 6-CF<sub>3</sub>); for **18c**  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 7.24 (1 H, m, 4'- and 4''-ArH), 7.40 (2 H, m, 3'-, 3'', 5'- and 5''-ArH) and 7.50 (2 H, m, 2'-, 2'', 6'- and 6''-ArH);  $\delta_{\text{F}}$ (235 MHz; CDCl<sub>3</sub>) –56.11 (1 F, q,  $J_{1,3a}$  13.3, 1- and 6-CF<sub>3</sub>), –56.45 (1 F, q,  $J_{3a,1}$  13.3, 3a- and 4a-CF<sub>3</sub>).

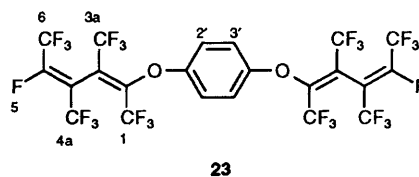


**Reaction of the Diene 1 with Benzene-1,4-diol 19.**—Benzene-1,4-diol **19** (0.3 g, 2.7 mmol) in diethyl ether (10 cm<sup>3</sup>) was added dropwise to a stirred mixture containing the diene **1** (2.0 g, 5.5 mmol), dry caesium carbonate (4.0 g, 12.3 mmol) and diethyl ether (30 cm<sup>3</sup>). After 4.5 d at room temperature, the solvent was removed, and molecular distillation of the residue (30 °C, 0.8 mmHg) gave a colourless liquid which crystallised at room temperature, and was identified as a 28:13:5:2 mixture of (Z,Z)-, (Z,E)-, (E,E)-, and (E,Z)-2-(4-hydroxyphenoxy)-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene **22a-d** (0.4 g, 32.5%). For the mixture (Found: C, 37.0; H, 1.2. C<sub>14</sub>H<sub>5</sub>F<sub>13</sub>O<sub>2</sub> requires

C, 37.2; H, 1.1%);  $\nu_{\max}/\text{cm}^{-1}$  1710w (C=C), 1670w (Ar), 1505m (Ar), 1360m (C–F) and 1300–1070s (C–F);  $\delta_{\text{H}}$ (400 MHz; (CD<sub>3</sub>)<sub>2</sub>CO) 7.36 (2 H, AB,  $J$  8.8, 2'-ArH), 7.32 (2 H, AB,  $J$  8.8 3'-ArH) and 2.84 (br s, OH);  $m/z$  452 (M<sup>+</sup>, 7%), 451 (M<sup>+</sup>–1); for **22a**  $\delta_{\text{F}}$ [376 MHz; (CD<sub>3</sub>)<sub>2</sub>CO] –61.12 (3 F, s, 3a-CF<sub>3</sub>), –62.34 (3 F, s, 1-CF<sub>3</sub>), –61.26 (3 F, d,  $J_{4a,5}$  16.2, 4a-CF<sub>3</sub>), –69.51 (3 F, s, 6-CF<sub>3</sub>) and –104.76 (1 F, m, 5-CF); for **22b**  $\delta_{\text{F}}$ [376 MHz; (CD<sub>3</sub>)<sub>2</sub>CO] –58.14 (3 F, m, 3a-CF<sub>3</sub>), –63.50 (3 F, q,  $J_{1,3a}$  6.8, 1-CF<sub>3</sub>), –60.56 (3 F, d,  $J_{4a,5}$  15.4, 4a-CF<sub>3</sub>), –70.54 (3 F, d,  $J_{6,5}$  7.2, 6-CF<sub>3</sub>) and –106.41 (1 F, m, 5-CF); for **22c**  $\delta_{\text{F}}$ [376 MHz; (CD<sub>3</sub>)<sub>2</sub>CO] –57.33 (3 F, q,  $J_{3a,1}$  9.0, 3a-CF<sub>3</sub>), –61.00 (3 F, s, 1-CF<sub>3</sub>), –63.50 (3 F, s, 4a-CF<sub>3</sub>), –69.25 (3 F, d,  $J_{6,5}$  10.5 of q,  $J_{6,4a}$  2.1, 6-CF<sub>3</sub>) and –100.03 (1 F, m, 5-CF); for **22d**  $\delta_{\text{F}}$ [376 MHz; (CD<sub>3</sub>)<sub>2</sub>CO] –56.99 (3 F, m, 3a-CF<sub>3</sub>), –63.30 (3 F, m, 1-CF<sub>3</sub>), –64.17 (3 F, d,  $J_{4a,5}$  3.8 of q,  $J_{4a,3a}$  1.9, 4a-CF<sub>3</sub>), –69.25 (3 F, s, 6-CF<sub>3</sub>) and –101.12 (1 F, m, 5-CF).

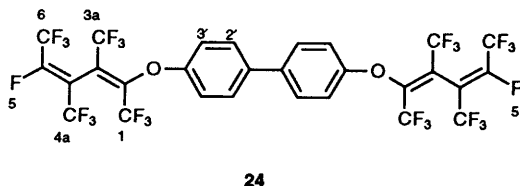


The remaining solid was purified by sublimation (50 °C, 0.8 mmHg) to give a white material, which was shown to be one product by NMR, and identified as p-phenylenedioxy-2,2'-bis[3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] **23** (1.25 g, 58%) (Found: C, 33.0; H, 0.5. C<sub>22</sub>H<sub>4</sub>F<sub>26</sub>O<sub>2</sub> requires C, 33.25; H, 0.5%);  $\nu_{\max}/\text{cm}^{-1}$  1710w (C=C), 1665w (Ar), 1505m (Ar), 1360m (CF) and 1330–1050s (CF);  $\delta_{\text{H}}$ (400 MHz; CDCl<sub>3</sub>) 7.02 (s, 2'- and 3''-ArH);  $\delta_{\text{F}}$ (376 MHz; CDCl<sub>3</sub>) –60.52 (6 F, d,  $J_{4a,5}$  16.2, 4a-CF<sub>3</sub>), –60.58 (6 F, s, 3a-CF<sub>3</sub>), –61.85 (6 F, s, 1-CF<sub>3</sub>), –68.93 (6 F, d,  $J_{6,5}$  4.1, CF<sub>3</sub>-6) and –104.16 (2 F, q,  $J_{5,4a}$  15.8 of q,  $J_{5,6}$  7.5, CF<sub>3</sub>-5);  $m/z$  794 (M<sup>+</sup>, 64%).



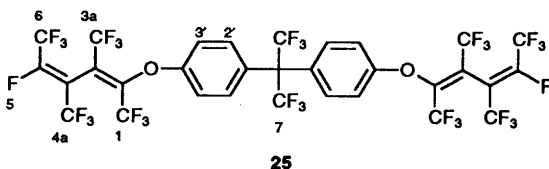
**Reaction of the Diene 1 with Biphenyl-4,4'-diol 22.**—A solution of biphenyl-4,4'-diol **20** (0.77 g, 4.1 mmol), in diethyl ether (5 cm<sup>3</sup>) and acetone (5 cm<sup>3</sup>), was added dropwise to a mixture of the diene **1** (3.00 g, 8.3 mmol), caesium carbonate (5.400 g, 16.6 mmol) and acetonitrile (30 cm<sup>3</sup>). After the mixture had been stirred for 72 h at room temperature, the resulting solid was filtered off, and the filtrate evaporated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) and the solution dried (MgSO<sub>4</sub>) and evaporated under reduced pressure; the residue was sublimed *in vacuo* (80 °C, 0.05 mmHg) to give a white solid which was identified as (biphenyl-4,4'-diyldioxy)-2,2'-bis[3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene] **24** (2.8 g, 78%) (Found: C, 38.8; H, 0.85. C<sub>28</sub>H<sub>8</sub>F<sub>26</sub>O<sub>2</sub> requires C, 38.6; H, 0.9%);  $\nu_{\max}/\text{cm}^{-1}$  1705w (C=C), 1665w (Ar), 1607w (Ar), 1495m

(AR), 1360m (CF) and 1330–1090s (CF);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 7.06 (4 H, AB,  $J$  8.6, 3'-ArH) and 7.55 (4 H, AB,  $J$  8.6, 2'-ArH);  $\delta_{\text{F}}$  (376 MHz;  $\text{CDCl}_3$ ) -60.41 (6 F, d,  $J_{6,5}$  23.7, 4a-CF<sub>3</sub>), -60.51 (F, s, 3a-CF<sub>3</sub>), -61.75 (6 F, s, 1-CF<sub>3</sub>), -68.91 (6 F, s, 6-CF<sub>3</sub>) and -104.26 (2 F, m, 5-CF);  $m/z$  870 ( $\text{M}^+$ , 63%).



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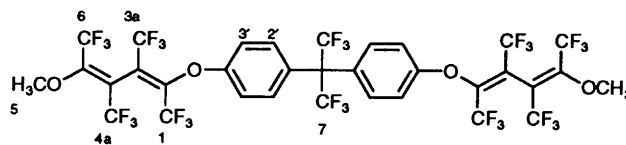
**Reaction of the Diene 1 with 2,2-Di(4-hydroxyphenyl)-hexafluoropropane 23.**—A solution of 2,2-di(4-hydroxyphenyl)hexafluoropropane **21** (1.39 g, 4.1 mmol) in acetonitrile (10 cm<sup>3</sup>) was added dropwise to a stirred mixture of the diene **1** (3.00 g, 8.3 mmol), caesium carbonate (5.40 g, 16.6 mmol) and acetonitrile (30 cm<sup>3</sup>). After 12 d at room temperature, the solid was filtered off, extracted with acetone and the extract dried ( $\text{MgSO}_4$ ). Evaporation of the extract under reduced pressure gave a residue which was sublimed *in vacuo* (80 °C, 0.10 mmHg) to give a white solid, which crystallised from acetone as white needles, and was subsequently identified as *bis*(trifluoromethyl)-methylenedi-*p*-phenylenedioxy-2,2'-bis[3,4-bis(trifluoromethyl)-perfluorohexa-2,4-diene] **25** (3.5 g, 83%) (Found: C, 36.8; H, 0.7.  $\text{C}_{31}\text{H}_8\text{F}_{32}\text{O}_2$  requires C, 36.5; H, 0.8%;  $\nu_{\text{max}}/\text{cm}^{-1}$  1710w (C=C), 1670w (Ar), 1607m (Ar), 1515m (Ar), 1360m (CF) and 1330–1090s (CF);  $\delta_{\text{H}}$  [400 MHz;  $(\text{CD}_3)_2\text{CO}$ ] 7.31 (4 H, AB,  $J$  8.8, 2'-ArH) and 7.62 (4 H, AB,  $J$  8.8, 3'-ArH);  $\delta_{\text{F}}$  [376 MHz;  $(\text{CD}_3)_2\text{CO}$ ] -61.14 (12 F, s, 1- and 3a-CF<sub>3</sub>), -62.62 (6 F, s, 4a-CF<sub>3</sub>), -64.63 (6 F, s, 7-CF<sub>3</sub>), -69.53 (6 F, s, 6-CF<sub>3</sub>) and -104.53 (2 F, m, 5-CF);  $m/z$  1020 ( $\text{M}^+$ , 92%) and 951 ( $\text{M}^+ \pm 69$ ).



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**Reaction of the Diene 27 with Sodium Methoxide.**—A solution of sodium methoxide (0.20 g, 3.7 mmol) in methanol (5 cm<sup>3</sup>) was added to the diene **25** (0.20 g, 0.2 mmol) and methanol (10 cm<sup>3</sup>) and the mixture stirred at room temperature for 48 h. Removal of the solvent gave a residual solid which was extracted with diethyl ether and the extract dried ( $\text{MgSO}_4$ ). Subsequent solvent removal from the extract and recrystallisation of the residue from acetone, gave an off-white solid which was identified as *bis*(trifluoromethyl)methylenedi-

*p*-phenylenedioxy-2,2'-bis[5-methoxy-3,4-bis(trifluoromethyl)-perfluorohexa-2,4-diene] **26** (0.15 g, 73%), m.p. 116 °C (Found: C, 38.1; H, 1.4.  $\text{C}_{33}\text{H}_{14}\text{F}_{30}\text{O}_4$  requires C, 37.9; H, 1.3%;  $\nu_{\text{max}}/\text{cm}^{-1}$  2975w (CH), 1700w (C=C), 1655w (Ar), 1610w (Ar), 1513m (Ar), 1350m (CF) and 1325–1065s (CF);  $\delta_{\text{H}}$  (376 MHz;  $\text{CDCl}_3$ ) 3.99 (3 H, s, 5-CH<sub>3</sub>), 7.01 (2 H,  $J_{\text{AB}}$  8.4, 2'-ArH) and 7.39 (1 H,  $J_{\text{AB}}$  8.4, 3'-ArH);  $\delta_{\text{F}}$  (376 MHz;  $\text{CDCl}_3$ ) -60.20 (1 F, s, 3a-CF<sub>3</sub>), -60.96 (1 F, s, 1- or 4-CF<sub>3</sub>), -61.95 (1 F, s, 1- or 4a-CF<sub>3</sub>), -63.58 (1 F, s, 6-CF<sub>3</sub>) and -64.02 (1 F, s, 7-CF<sub>3</sub>);  $m/z$  1044 ( $\text{M}^+$ , 34%).



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### Acknowledgements

We thank the following for financial support: The Daikin Co., Japan (to T. N.), the Science and Engineering Research Council and E. A. Technology for CASE support (to M. W. B., S. J. M., and J. F. S. V.).

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Paper 4/03820G

Received 23rd June 1994

Accepted 25th July 1994